METHODS FOR FABRICATING METAL NANOWIRES

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CROSS-REFERENCE TO RELATED APPLICATION

This application is related to provisional U.S. Patent Application Serial No. 60/306,715 and Provisional U.S. Patent Application Serial No. 60/317,862, which applications are fully incorporated herein by reference.

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FIELD OF THE INVENTION

The invention relates to metal nanowires and, more particularly, to methods which facilitate the fabrication of long, free standing metal nanowires.

BACKGROUND

15   Metal nanowires have great potential for immediate use in small electronic circuits, sensitive chemical sensors or any application requiring metal filaments, and will likely be required as interconnects in the nanometer-scale electronics of the future, especially those future electronics which are not based on existing silicon technology. However, there are few methods for preparing nanowires that have such

20   technological utility. More particularly, few methods are capable of producing

nanowires that are long (i.e., greater than ten microns in length), uniform in diameter, free standing, and metallic. Two of the most successful approaches have been *template synthesis* and *step-edge decoration*.

The *template synthesis* method, which is described in publications by the

5 research groups of M. Moskovits[16-18], C.R. Martin[8-15], and P.C. Searson[21-27], appears to permit the growth of metal nanowires over a wide range of diameters (from nanometer to micron scale) and for a variety of different metals. *Template synthesis* involves the growth of carbon, metals, or polymers in the void volumes of a nonconductive porous host such as polycarbonate ultrafiltration membranes, porous Al_2O_3 films, and track-

10 etched mica crystals all of which possess long (microns or longer), dimensionally uniform pores. In general, these pores are oriented perpendicular to the plane of the porous film or membrane. Nanowires are produced by filling these pores with a conductive material. *Template synthesis*, however, is limited by its reliance on a template. Because all of the templates listed above possess linear, cylindrical (or

15 prismatic) pores, only linear nanowires can be produced. Moreover, nanowires produced by *template synthesis* are limited to a maximum length that is equal to the thickness of the porous host membrane, which tends to range from 0.1 to 20 microns.

The *step edge decoration* method, which is described in publications by Himpsel[3-4], Kern[5-7], Behm[2] and others, involves the selective deposition of a metal or

20 other material, such as CaF_2, at atomic step edges on a vicinal single crystal surface.

Step edge decoration can be controlled to yield continuous "wires" of varied width and interwire spacing. Long nanowires that are many microns in length have been prepared. Because the dimension of the "wire" perpendicular to the vicinal surface has usually been limited to one or at most two atomic layers, it has not been possible

5   to remove these ultra thin metallic ribbons from the surfaces on which they are synthesized. The technological utility of such nanowires is necessarily limited as a result.

In view of the foregoing, it would be desirable to provide methods that facilitate the fabrication of nanowires that are metallic, long (i.e., greater than ten microns in

10   length), uniform in diameter, and removable from the surface on which they are synthesized and, thus, free standing.

SUMMARY OF INVENTION

The present invention is directed to methods that facilitate the fabrication of nanowires that are metallic, long (i.e., greater than ten microns in length), uniform in

15   diameter, and removable from the surface on which they are synthesized and, thus, free standing. The fabrication processes of the present invention provide an electrochemical route to dimensionally uniform and mechanically robust metal nanowires that range in diameter from approximately 10-15 nm to approximately 1.0 μm, and are up to approximately 1.0 mm or more in length. The metal nanowires

20   produced by the methods of the present invention advantageously exhibit wire

diameter uniformity along the length of the wire as well as from wire-to-wire for

thousands of nanowires. Preferably, the relative standard deviation from a mean

diameter tends to be in a range of about 5 to 20 %, and more preferably is no more

than about 10%. In addition, the metal nanowires produced by the methods of the

5   present invention tend to be electrically continuous along their entire length, i.e.,

typically less than about 5% of the wires produced by the methods of the present

invention tend to show any visible breaks.

The present invention includes three interrelated step-decoration methods that

are based on the selective electrodeposition of a metal or metal oxide from an aqueous

10   solution at step edges present on a basal plane-oriented surface, such as graphite, that

is exposed to the solution. In a first innovative aspect of the present invention (Method

I), metal oxide from an aqueous solution is selectively electrodeposited along step

edges present on the stepped surface to form precursor metal oxide wires. The metal

oxide nucleates at a high linear density along the step edges forming beaded chains of

15   metal oxide nuclei, which, with continued deposition, rapidly grow into a

hemicylindrical nanowires. Wire growth involves low overpotential deposition at

constant, or nearly constant, deposition current. Once formed, the precursor metal

oxide nanowires are preferably reduced in hydrogen gas (H_2) at elevated temperatures

to produce metal nanowires. Preferably this gas phase reduction occurs at about 500°

20   C for about an hour.

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In a second innovative aspect of the present invention (Method II), metal nanowires are prepared by direct electrodeposition of metal from an aqueous solution along step edges present on a stepped surface exposed to the solution. Following a nucleation pulse, the metal nucleates at a high linear density along the step edges

5   forming beaded chains of metal nuclei, which, with continued deposition, grow into hemicylindrical nanowires. Wire growth involves low overpotential deposition at constant, or nearly constant, low deposition current. The deposition rates according to this method are preferably extremely low, e.g., the deposition rate to prepare a palladium nanowire via direct electrodepositon having a 200 nm diameter was about

10   10 minutes and a 300 nm diameter was about 20 minutes.

In a third innovative aspect of the present invention (Method III), beaded or hybrid metal nanowires comprising a first metal (metal A) into which nanoparticles of a second metal (metal B) have been inserted are prepared by first electrodepositing nanoparticles of metal B selectively along step edges of a step surface. The metal B

15   nanoparticles are then capped with a molecular layer of an organic ligand having a strong affinity for the surface of the metal B nanoparticles. Metal A is then selectively electrodeposited along the step edges separating each metal B nanoparticle according to Method I or II. The ligand layer is preferably removed by heating the surface under reducing conditions in order to retain the metallic composition of the particles and

20   connecting nanowire segments. The nanoparticles incorporated into the nanowires

may range in diameter from the diameter of the nanowire itself, e.g., as small as about

10 nm, to about 1.0 μm or more.

In all three methods, the nanowires may be removed from the graphite surface

by embedding the wires in a polymer film, and then pealing this film containing the

5   embedded nanowires off of the graphite surface. This removal step makes the

nanowires available for electrical characterization, for use as interconnects for

connecting two nanometer-scale elements of a circuit, for the implementation of a

variety of nanowire-based devices including sensors and biosensors, and for wiring of

semiconductor quantum dots[20] to form a circuit. When used in sensors, the binding of

10   an analyte molecule to the surface of the nanowire induces a measurable change in

the nanowire conductivity.

Other objects and features of the present invention will become apparent from

consideration of the following description taken in conjunction with the accompanying

drawings.

15   BRIEF DESCRIPTION OF DRAWINGS

Figure 1 is a schematic diagram of Method I of the present invention for

preparing metallic nanowires.

Figure 2 is a schematic diagram of a nanometer scale electric circuit

incorporating an ensemble of metallic nanowires prepared in accordance with the

20   methods of the present invention.

Figure 3 is a series of scanning electron microscope images of molybdenum nanowires prepared in accordance with Method I of the present invention.

Figure 4 is a typical cyclic voltammogram for MoO_4^{2-} at a highly oriented pyrolytic graphite electrode and scanning electron microscope images (above the

5   cyclic voltommogram) of graphite surfaces obtained following the deposition of molybdenum dioxide (MoO_2).

Figure 5 includes scanning electron microscope images of molybdenum nanowires embedded in a polystyrene film after removal from a graphite surface.

Figure 6 is a schematic diagram of Method II of the present invention for

10   preparing metallic nanowires by direct electrodeposition of a metal.

Figure 7 includes cyclic voltommograms for a graphite electrode in two aqueous palladium plating solutions.

Figure 8 is a graph showing the diameters of palladium nanowires as a function of the deposition time for nanowires deposited using the plating solutions indicated in

15   figure 7.

Figure 9 includes scanning electron micrographs of palladium nanowires prepared by electrodeposition from aqueous solutions indicated in figure 7.

Figure 10 includes scanning electron micrographs of 300 nanometer diameter palladium nanowires prepared in accordance with Method II of the present invention.

20   Figure 11 is a schematic diagram of Method III of the present invention for

preparing hybrid or beaded metal nanowires.

Figure 12 is a scanning electron micrograph image of a graphite surface following the implementation of the first three steps of Method III of the present invention.

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DESCRIPTION

Referring in detail to the figures, methods that facilitate the fabrication of metallic nanowires and metallic nanowires prepared in accordance with the methods the present invention are shown. The methods of the present invention involve

10 fabrication processes that provide an electrochemical route to dimensionally uniform, mechanically robust, long metal nanowires that are removable from the surface on which they are synthesized and, thus, free standing. The metal nanowires produced by the methods of the present invention tend to range in diameter from approximately 10-15 nm to approximately 1.0 μm and tend to be greater than 10-20 μm in length and

15 preferably hundreds of microns in length on up to approximately 1.0 mm or more in length. The metal nanowires also advantageously exhibit high wire diameter uniformity along the length of the wire as well as from wire-to-wire for thousands of wires with a standard relative deviation from a mean diameter preferably in a range of about 5 to 20 % and more preferably no more than about 10%. In addition, the metal

20 nanowires produced by the methods of the present invention tend to be electrically

continuous along their entire length, i.e., typically less than about 5% of the wires

produced by the methods of the present invention tend to show any visible breaks.

The methods of the present invention include three interrelated step-decoration

fabrication processes that are based on the electrodeposition of a metal or metal oxide

5   from an aqueous solution on a basal plane-oriented surface, such as graphite, that is

exposed to the solution. When suitable electric overpotentials are applied to the

aqueous solution, the metal or metal oxide contained therein selectively deposits

along the step edges present on the stepped surface forming "beaded-chains" of nuclei.

With continued deposition, the beaded chains form three-dimensional nanowires with

10   diameters in a range of about 10-15 nm to 1.0 μm for metal and in a range of about

20nm to 1.3 μm for a metal oxide. The length of the nanowires tend to equal the

length of the step edges on the stepped surface, which, with graphite in particular,

tend to be equal to the grain diameter.

A first embodiment of the present invention, i.e., Method I, shown

15   schematically in figure 1, includes a first step (Step 1) wherein precursor nanowires 14

are selectively electrodeposited along the step edges 12 present on a stepped surface

10 from a dilute, preferably alkaline (pH of approximately 8.5), aqueous plating

solution. The plating solution preferably includes an electrodepositable metal oxide at

concentrations between about $1 \times 10^{-3}M$ and about $10 \times 10^{-3}M$ of the metal ion of

20   interest. The metal oxide in the plating solution tends to nucleate at an extremely high

linear density, i.e., greater than approximately 20 nuclei/micron, along the step edges

12 forming "beaded chains" of metal oxide nuclei. With continued deposition, these

beaded chains rapidly become smooth, hemicylindrical precursor nanowires 14. As

deposited, the precursor nanowires 14 tend to be brittle and nonconductive, but are

5   highly uniform in diameter, with diameters in the range of about 20 nm to 1.3 µm, and

tend to be hundreds of microns to about 1.0 mm or more in length.

Method I of the present invention includes a second step (Step 2) which

involves a gas phase reduction of the precursor metal oxide nanowires 14 at elevated

temperatures. Preferably, the metal oxide nanowires 14 are reduced in hydrogen gas

10   (H_2) at about 500° C for about one hour to produce metallic nanowires 16 that retain

the dimensional uniformity and hemicylindrical shape of the precursor, or "parent",

metal oxide composite nanowires 14. The metallic nanowires 16 tend to be smaller in

diameter (about 10-15 nm to 1 µm) than the parent nanowires 14 by about 30 to 35%,

and tend to be mechanically resilient and electronically conductive.

15   In a third step (Step 3) of Method I, the gas phase reduced metal nanowires 16,

which tend to be only weakly associated with the stepped surface 10, are embedded in

a thin polystyrene film 18 that is cast onto the nanowires 16 and the graphite surface

10. In a fourth step (Step 4) of Method I, the film 18, after it is allowed to air dry, is

peeled off of the graphite surface 10 with the metal nanowires 16 embedded therein.

20   The embedded nanowires 16 may comprise an ensemble of tens to hundreds of

nanowires or more. The ensemble of nanowires 20, which have been removed from

the graphite surface 10 and, thus, are free standing, may advantageously be

incorporated into an electronic circuit or sensor 22 as shown in figure 2. Low

impedance electrical contacts 24 of silver, evaporated gold film and the like, may be

5   connected to the ends of the nanowires 20.

Referring back to Figure 1, the system used for electrodeposition, i.e. Step 1,

preferably includes a glass electrochemical cell having a volume of approximately 50

mL. The plating solution noted above is introduced into the cell along with three

electrodes: A platinum "counter" electrode, a reference electrode (e.g., saturated

10   calomel electrode), and a "working" electrode, which is the surface, such as graphite,

on which the nanowires are to be grown. The two additional electrodes - i.e., the

counter and reference electrodes - enable high precision control of the potential of the

working electrode. All three electrodes are preferably connected to a three-electrode

potentiostat (e.g., EG&G Model 273A) which may be programmed to apply the

15   required potential to the working electrode.

The selective decoration of the step edges 12 and, thus, wire growth, in Step 1

occurs when the deposition is carried out at suitable overpotentials, η_{dep} (where η_{dep} =

$E_{dep} - E_{eq}$). Suitable overpotentials, η_{dep}, used in Step 1 for wire growth may range up

to about (-)900mV versus the reversible potential[1], E_{eq}, of the specific material

20   involved. If the deposition is carried out using larger overpotentials, nucleation tends

to be spatially indiscriminant and metal oxide particles tend to be deposited everywhere on the surface of the step terrace 13. Moreover, if the overpotentials are too large, nucleation tends to occur on the surface of the step terrace 13 to the exclusion of the step edges 12.

5   The deposition process of Step 1 is preferably further characterized by the application of a constant, or nearly constant, deposition current over the deposition period, which is typically greater than 20 seconds to grow nanowires of a desired size. Preferably, the constant deposition current is in a range of about 10 to 200 microamps/cm^2 of electrode area. This rate invariance is consistent with a convection

10   limited growth process where natural convective mixing of the electrolyte near an electrode surface occurs. Under these conditions the rate law for growth of a hemicylindrical solid becomes

$$r(t) = (2 i_{dep} t_{dep} M / \pi\, n\, F\, \rho\, L)^{1/2} \qquad\qquad (1)$$

where r(t) is the radius of the hemicylindrical nanowire, i_{dep} is the deposition current,

15   t_{dep} is the deposition time, M is the atomic weight of the deposited metal, n is thenumber of electrons transferred per metal atom, F is the Faraday constant, i.e., 96,485 C eq^{-1}, ρ is its density, and L is the total length of the nanowire(s) on the electrode surface. As indicated by Equation 1, the nanowire diameter is directly proportional to the square root of the deposition time. As a result, nanowires of a

20   particular diameter can be selectively produced by the methods of the present

invention. Further, because *dr/dt* is proportional to $t^{-1/2}$, the growth of highly

dimensional uniform structures, i.e., populations of nanowires that are narrowly

dispersed with respect to wire diameter, is possible.

As indicated above, the diameter of the precursor nanowires 14 range from

5   about 20 nm to 1.3 μm, which is typically many times the height of the step edge 12

responsible for nucleating the growth of the wire 14. The height of the step edge 12 is

typically about 0.3 to 2.0 nm. Two factors tend to contribute to this "amplification" of

the step edge 12. First, at the low deposition potentials used in the methods of the

present invention, the incipient nucleation sites tend to be confined to the step edges

10   12 on the graphite surface 10, which helps prevent the "spread" of the nanowire 14

onto terraces 13 during growth. The second factor is the inherent hemicylindrical

symmetry of diffusional transport to metal nuclei arrayed along a linear step. The

nanowire 14 ends up with a hemicylindrical cross-section because the ionic transport

to the surface of the growing wire has this symmetry. These two factors operate in

15   concert and permit the growth of hemicylindrical wires with virtually any diameter

from step edges having molecular dimensions.

It should be understood that Method I may be used to produce metal nanowires

from any conductive metal oxide that is electrodepositable, including MoO_2, Cu_2O,

Fe_2O_3, and the like. The fabrication of molybdenum nanowires is described below

20   with regard to figures 3-5 for exemplary purposes only. See also Zach et al., *Science*

290 (2000) 2120[28], which is incorporated by reference as if set forth in full.

To prepare molybdenum nanowires in accordance with Method 1 shown in

figure 1, molybdenum dioxide (MoO_2) is first electrodeposited (Step 1) according to

the reaction:

5 · $$MoO_4^{2-} + 2H_2O + 2e^- \rightarrow MoO_2 + 4OH^-$$ (2)
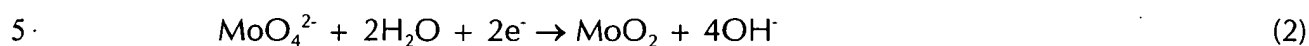
Under the conditions employed in Step 1, i.e., low overpotentials in a range of

about -600 mV to -800mV and constant, or nearly constant, deposition current in a

range of about 10 to 200 microamps/cm^2, MoO_2 nucleates at an extremely high linear

density (greater than about 20 nuclei/μm) along the step edges 12. The deposited

10   MoO_2 forms "beaded chains" of 5-8 nm diameter MoO_2 nuclei which, with continued

deposition, rapidly become smooth, hemicylindrical nanowires. Figure 3 shows a

series of MoO_2 nanowires electrodeposited according to Step I of Method 1 along step

edges of a stepped graphite surface. As shown in figure 3, the MoO_2 nanowires

include nanowires with diameters of 13 nm, 62 nm, 130 nm and 210nm. The

15   numbers at the upper left indicate the deposition time, in seconds, i.e., 1s, 4s, 16s, and

256s, for preparing these MoO_2 nanowires from an aqueous solution containing 1.0

mM MoO_4^{2-} by applying a deposition potential of about -0.75 V vs. SCE.

A typical cyclic voltammogram for MoO_4^{2-} at a highly oriented pyrolytic

graphite electrode is shown in figure 4. As figure 4 indicates, the selectivity of MoO_2

20   nucleation is controlled by the deposition potential. The scanning electron

microscopy (SEM) images (above the cyclic voltammogram) of the graphite surfaces

were obtained following deposition at potentials in a range of about (-)0.7 to (-)0.9 V

versus a saturated calomel electrode (SCE) (right) and in a range of about (-)1.25 to (-

)1.4 V versus SCE (left). As shown, electrodeposition of MoO_x, which has a reversible

5   potential of about 0.1V, occurred with a high degree of selectivity at step edges at

deposition overpotentials in the range of (-)0.6 to (-)0.8 V versus SCE (right). The

application of a deposition potential more negative than (-) 1.0 V (left) caused particle

growth at surface terraces.

Once formed, MoO_x nanowires may be reduced in H_2 at 500°C to produce

10   metallic molybdenum (Mo^0) nanowires (Step 2). These metal nanowires are smaller in

diameter by about 30% to 35% as compared with the parent MoO_x wires, and are only

weakly associated with the graphite surface 10. Removal of these reduced wires from

the graphite surface is accomplished by embedding the nanowires in a polystyrene

film (Step 3), and lifting this film together with the embedded nanowires off the

15   graphite surface (Step 4). Figure 5 provides SEM images of molybdenum nanowires

embedded in a polystyrene film after removal from a graphite surface. The ability to

remove molybdenum nanowires from the graphite surfaces on which they are

synthesized facilitates the technological utility of these nanostructures both in

electronic devices, as interconnects, and in sensors.

20   Turning to figure 6, a second embodiment of the present invention, Method II,

is shown schematically to involve the preparation of metal nanowires by "direct"

electrodeposition of a metal on a stepped surface 110, such as graphite, that is

exposed to an aqueous solution containing the metal. In a first step (Step 1),

nanowires 116 are selectively electrodeposited along the step edges 112 present on a

5   stepped surface 110 from an aqueous plating solution comprising a electrodepositable

metal. The solution preferably includes metals such as palladium, gold and the like, at

concentrations between about 1×10^{-3} and $10 \times 10^{-3}M$ of the metal ion of interest.

Electrodeposition of gold, however, is preferable performed in an electrochemical cell

that is pressurized to about 40 atm. Following a nucleation pulse, the metal in the

10   plating solution nucleates at an extremely high linear density (i.e., greater than about

$20/\mu m$) along the step edges 112 forming "beaded chains" of metal nuclei, which,

with continued deposition, become smooth, hemicylindrical nanowires 116.

Preferably, the electrodeposition is carried out at very low deposition

overpotentials of up to about (-)400mV and preferably in a range of about (-)10 to

15   (-)200mV. To increase nucleation density and , thus, ensure that the nanowires are

continuous, a nucleation pulse, well negative of the reversible potential, may be

applied for about five milliseconds prior to electrodeposition at the desired

overpotential. The deposition is preferably carried out at low constant, or nearly

constant, deposition current, e.g., preferably less than $50mA/cm^2$. Depending on the

20   metal being deposited and the applied current density, which is preferably in a range

of about $5\mu Acm^{-2}$ to $50\mu Acm^{-2}$, the deposition rates in Method II are preferably

extremely low. For example, as shown in figure 8 and discussed below, the

deposition time to prepare a palladium nanowire having a 200 nm diameter was about

ten minutes. Deposition rates to prepare metal nanowires of a desired diameter may

5   be determined according to Method II may be calculated using Equation (1).

In a second step (Step 2) of Method II, the metal nanowires 116 are embedded

in a thin polystyrene film 118 that is cast onto the nanowires 116 and the graphite

surface 110. In a third step (Step 3), the film 118, after it is allowed to air dry, is

peeled off of the graphite surface 110 with the metal nanowires 116 embedded

10   therein. The embedded nanowires 16 may comprise an ensemble of tens to hundreds

of nanowires or more. The ensemble of nanowires, which have been removed from

the graphite surface 110, may also advantageously be incorporated into an electronic

circuit or sensor 22 as shown in figure 2.

Palladium nanowires prepared in accordance with Method II are described in

15   regard to figures 6-10 for exemplary purposes only. Palladium nanowires may be

electrodeposited from aqueous solutions containing palladium. Examples of such

solutions include 2.0 mM Pd^{2+}, 0.1 M HCl, water, and 2.0 mM Pd^{2+}, 0.1 M $HClO_4$,

and the like. Palladium nanowires prepared by the process of Method II are shown in

figures 9-10. Starting with a freshly cleaved graphite surface within a palladium

20   plating solution, these nanowires were prepared by first applying a 5 ms nucleation

pulse of –0.2 V (vs. saturated calomel electrode, SCE). As shown in figure 7, this

potential is well negative of the reversible potential for palladium deposition in these

solutions (+0.6 to +0.7 V vs. SCE). After this nucleation pulse, the growth of

palladium nanowires was carried out using potentials in the ranges shown in gray in

5   figure 7. These deposition potentials produce deposition current densities ranging

from about 30-60 μA cm^{-2} and deposition times for 200 nm diameter wires of about 10

minutes (see figure 8). The deposition times for palladium nanowires having 300 nm

diameters, as shown in figure 10, were about 20 minutes.

The morphology of the palladium nanowires, as well as other metal nanowires,

10   obtained by electrodeposition tends to be dependent on the identity of the electrolyte

present in the plating solution. For example, palladium nanowires deposited from HCl

solutions, as shown in figure 9 (left), tend to be rough and granular. The dimensions of

the grains in these polycrystalline wires as estimated from SEM images ranged from

about 50 to 300 nm. Continuous nanowires of 150 nm in diameter have been

15   obtained from this solution. Deposition of palladium nanowires from HClO$_4$ solutions

as shown in figure 9 (right), yield nanowires having a smoother morphology. The

grains in these nanowires were 10-50 nm in diameter. A smoother morphology

permits nanowires as narrow as 55 nm in diameter to be deposited. The rough and

smooth nanowires prepared using these two plating solutions behave electrically

20   identical to one another.

A third embodiment of the present invention, Method III, involves the

preparation of beaded or hybrid metal nanowires comprising a first metal (metal A)

into which nanoparticles of a second metal (metal B) have been inserted. These hybrid

metal nanowires are prepared, as shown schematically in figure 11, by first (Step 1)

5 electrodepositing nanoparticles 215 of metal B selectively along step edges 212 of a

stepped surface 210 such as graphite. The metal B nanoparticles 215, which are

preferably formed from a noble metal including nickel, palladium, platinum, gold, and

the like, are electrodeposited, e.g., from an aqueous solution comprising 1.0×10^{-3}m to

10×10^{-3}m of the metal ion of interest using a suitable overpotential. Platinum

10 nanoparticles, for example, are preferably deposited for 100ms from a 1.0×10^{-3}m pt^{2t}

solution using an overpotential of −0.5V in order to obtain 10nm diamter metal

nanoparticles at a density of about 10^8 to 10^{10} cm^{-2}. See, e.g., Zach et al., *Adv. Mat.,*

12 (2000) 878[29] and Zoval et al., *J. Phys. Che. B.* **102** (1998) 1166[30], and others which

are incorporated by reference as if set forth in full.

15 The deposited metal B nanoparticles 215 are then (Step 2) exposed to an

ehanolic solution of an aklane thiol. As a result of the thiol exposure, each

nanoparticle is "capped" by a self assembled molecular monolayer of an organic

ligand 217 having a strong affinity for the surface of the metal B nanoparticles 215.

Examples of such lygands include Thiols (chemical formula: R-SH where R is a

20 hydrocarbon), which have an affinity for noble and coinage metals including Pt, Pd,

Au, Ag, and Cu, and Nitriles (chemical formula: R-CN where R is a hydrocarbon),

which have an affinity for Pt, Pd and Ag.

In a next step (Step 3), a metal A or a metal A oxide is selectively

electrodeposited along the step edges 212 separating each metal B nanoparticle 215

5   according to Method I or II discussed above to form a metal A or metal A oxide

nanowire 214, 216 between the metal B nanoparticles 215. Because the ligand 217

forms an electrically insulating layer atop of the metal nanoparticles 215, the

deposition of the wire material does not occur on top of the nanoparicles 215, just

between the nanoparticles 215.

10   In a final step (Step 4), the ligand layer 227 is preferably removed by heating

the surface under reducing conditions in order to retain the metallic composition of the

particles 215 and connecting nanowire segments 216. Preferably, the reduction of the

surface occurs in H_2 at 500° C, which results in the alkane thiol being pyrolyaed. The

nanoparticles incorporated into the nanowires may range in diameter from the

15   diameter of the nanowire itself, e.g., as small as about 10 nm, to about 1.0 μm or

more. Figure 12, which is a SEM image of a graphite surface following Step 3 of

Method III, shows hybrid nanowires comprising nickel nanoparticles and molydbenum

dioxide nanowire segments prepared according to Method III.

Like the metal nanowires prepared according to Methods I and II (see figures 1

20   and 6), the hybrid nanowires prepared according to Method III may be removed from

the graphite surface by embedding the wires in a polymer film, and then pealing this

film containing the embedded nanowires off of the graphite surface. Because the

hybrid nanowires are removable they may be utilized as elements of nanometer-scale

circuits, sensors, biosensors, and the like. When used in sensors, the nanowire

5   segments are employed to "read-out" any measurable change in the nanoparticle

conductivity induced by the binding of an analyte molecule to the surface of the

nanoparticle.

While the invention is susceptible to various modifications and alternative

forms, specific examples thereof have been shown in the drawings and are herein

10   described in detail. Many alterations and modifications can be made by those having

ordinary skill in the art without departing from the inventive concepts contained

herein. It should be understood, therefore, that the illustrated embodiments have been

set forth only for the purposes of example and that they should not be taken as limiting

the invention.

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